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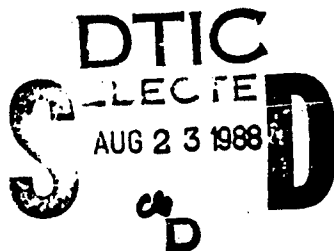
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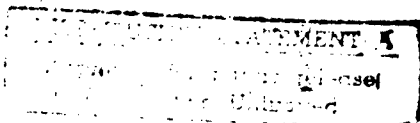
Literature Review of Inhibition for  
Vanadate Attack

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TABLE OF CONTENTS

	<u>Page</u>
I. INTRODUCTION .....	1
A. Alloy History .....	2
B. Hot Corrosion .....	3
1. Sulfidation Corrosion .....	3
a. Characterization .....	3
b. Salt Deposition .....	4
c. Sulfidation Corrosion Mechanisms .....	6
d. Sulfidation Inhibition .....	7
2. Vanadium Corrosion .....	8
a. Gaseous $V_2O_5$ .....	9
b. Condensed $V_2O_5$ .....	10
3. Condensed Alkali-Vanadates .....	11
4. Deposition and Inhibition Vanadium Corrosion...	12
II. DISCUSSION .....	14
Sulfidation .....	14
Vanadium .....	20
Vanadium-alkali .....	24
III. RECOMMENDATIONS .....	25



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## I. INTRODUCTION

Gas turbine engines are used as principle sources of power in air, marine and industrial environments. Entering air is compressed, fuel injected and the hot expanding gases travel through a turbine. As with all heat engines, its efficiency is related to the maximum and minimum temperature in a given cycle, and for increased efficiency and performance the trend is to continually increase the turbine inlet temperature. The turbine inlet temperature of the gas has increased from about 700°C in the early fifties to about 1350°C for today's engines (1). This high temperature is achieved not only through advances in metallurgy but through component cooling which was first introduced in the early sixties.

The turbine components operate under complex and demanding combinations of stress and temperature in a high-velocity gas stream which may contain corrosive compounds arising from contaminants in the fuel and air. Therefore, the materials must possess specific mechanical, physical as well as chemical properties to suit industrial requirements for specific areas of the engine.

The principal degradation mechanisms for the hot gas path components are creep, fatigue and corrosion. Creep is generally defined as the time dependent deformation that occurs under prolonged stressing at high temperature. Fatigue is the process through which components fail as a result of repeated applications of stress. Corrosion consists of (a) oxidation, the union of the surface with oxygen to form a scale which then limits the rate of consumption of the substrate and, (b) hot corrosion, the breakdown of the protective oxide scale by chemical interaction thereby accelerating the rate of consumption of the underlying substrate. The objective of this report is to review the pertinent literature with respect to vanadium-alkali corrosion in order to assess the feasibility of attenuating the hot corrosion in marine gas turbine engines.

### A. Alloy History

The current family of hot turbine alloys is based upon the growth and understanding of the mechanisms that are used to strengthen the Ni-20Cr alloy of the forties. It was discovered that the strength of the alloy could be increased by the precipitation of an ordered face centered cubic (FCC) phase designated gamma prime. This phase is rich in aluminum (and titanium) and has the general formula  $Ni_3(Al,Ti)$ . Further increases in mechanical properties are achieved through control of the grain boundary phases such as  $M_{23}C_6$ ,  $M_6C$  and MC. The volume fraction of the gamma prime phase was further increased after it was determined that the solubility of (Al+Ti) was increased by reducing the chromium content of the alloy. As the strength of the alloys increased and the gap between the solvus and solidus narrowed, forgings gave way to castings (2).

The mechanical properties of the cast alloys were further increased as the volume fraction of the gamma prime phase exceeded 60 v/o. However, full advantage of the excellent creep strength of these alloys such as Mar-M-200 could not be utilized because of reduced creep ductility. This problem was overcome by eliminating all the grain boundaries that make large angles with the stress axis. The sixties saw the introduction of the directionally solidified turbine alloy blades (3). Nevertheless, the demand for higher efficiencies eventually promoted the development of the latest family of blades which contain no intentionally added grain boundary strengthening elements thereby significantly increasing the incipient melting temperature of the alloy; and a higher gamma prime solvus for improved high temperature creep strength and reduced dendritic segregation, Fig. 1. These alloys are the single crystal alloys. Thus in the history of the development of the superalloys, oxidation and hot corrosion resistance received, in general, less attention than the mechanical and casting properties due primarily to the realization that the chemical properties of the alloy can be significantly improved through the use of protective coatings.

It should be noted that the early alloys owed their oxidation and corrosion resistance to the development of a protective  $\text{Cr}_2\text{O}_3$  oxide scale. This is the scale that forms on the Ni-20Cr alloy. However, as the chromium content falls below about 15 w/o, the oxide scale is no longer exclusively  $\text{Cr}_2\text{O}_3$  but contains various proportions of chromia depending upon both time and temperature. It is therefore apparent that during the development of the nickel base alloys, the oxidation and corrosion resistance of the alloy was undergoing a change. In general, as the chromium content of the alloy decreased and the aluminum content increased, the composition of the scale changed from chromium rich to spinels and most recently to an alumina rich scale.

## B. Hot Corrosion

### 1. Sulfidation Corrosion

#### a. Characterization

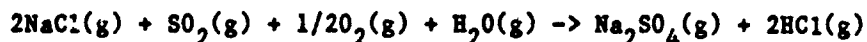
Sulfidation attack is a general term used to describe an accelerated rate of oxidation of alloys characterized by the presence of a non-protective oxide scale separated from the unaffected matrix by a zone containing numerous sulfide precipitates. Shirley (4) was among the earliest investigators to describe the sulfidation morphology associated with attack of Nimonic 80A alloy heater tubes used in peat burning turbines, and noted the similarities between the attacked Nimonic 80 alloy and corroded superheater supports from ocean liners which was later traced to sea water contamination of the fuel. In both cases, the alloys were coated with a deposit of sodium sulfate. In the fifties several examples of sulfidation attack in gas turbines were documented. Conde' (5), Archdal (6), Smith (7), and Llewellyn (8) described sulfidation attack of Nimonic 90 and Nimonic 100 alloy components removed from gas turbine powered patrol boats. In 1975 Stringer (9) compiled a voluminous report on the available sulfidation data for aircraft engines and numerous papers on the problems in marine and industrial gas turbines were presented in a series of meetings (10-14).

In general, the severity of the sulfidation attack in marine gas turbine engine increases with increasing temperature; but in some cases it was reported that the maximum corrosion appeared to be less on the very hottest parts of the blades. Carter (15) noted that the temperature of maximum attack for aluminized IN-738 components used in Olympus, Avon and Tyne engines is about 750°C and that this "low temperature sulfidation" is characterized by the absence of (a) the depletion zone, and (b) the presence of sulfide precipitates. A similar morphology was described by Fryxell et al (16) who noted that the LM2500 engines experience low temperature corrosion (below 750°C) and identified the sulfates of the substrate alloy as reaction products.

It is now generally agreed that sulfidation corrosion characterized by the presence of a non-protective oxide scale separated from the substrate by an alloy depleted zone containing sulfide precipitates is Type I sulfidation. Type II sulfidation is characterized by the absence of the depletion zone and sulfide precipitates. Whereas Type I is a broad-front attack, Type II is characterized by a pitting attack. Although Type I is generally believed to be the high temperature form of corrosion (>800°C), the temperature ranges of the two types of corrosion are believed to overlap.

#### b. Salt Deposition

The principal constituent of the salts associated with sulfidation corrosion is sodium sulfate. The source of the alkali is generally believed to be salts entering the gas turbine engine via the air or the fuel, and sulfur is a constituent of sea salt and a common impurity in the fuel. The two mechanisms by which material from the combustion gases can deposit on gas turbine components are vapor diffusion and condensed phase transport (23). M. DeCrescente and N. Bornstein were among the early investigators to note that in a gas turbine engine the reaction:



would be displaced very much to the right and Tschinkel (21) noted that the reaction



would also become important at high temperatures. Kohl et al (24) and Rosner et al (25, 26), have extensively considered the vaporization-condensation of sodium sulfate in a gas turbine. They found good agreement between maximum deposition rates predicted by mass transport consideration and the experimentally observed deposition rates in laboratory experiments.

It has also been postulated that in industrial and marine gas turbines, the compressor collects the salt as a deposit and fragments of the deposit may break-off intermittently and pass through the engine. This mechanism was first proposed by McCreath (27). Bornstein (28) determined the nature and amount of salt that adheres to the compressor of an industrial gas turbine engine and found that the composition of the salt present on the first few stages of the compressor is similar in composition to sea salt. Of significance is the observation that sodium sulfate is the major constituent of the salts present on the warmer compressor components and is the major constituent of the salt present on the hotter turbine components. It was hypothesized that the chemistry of the deposited salt onto the latter compressor stages is related to the solubility of the salt in the sea water droplet.

There is little doubt that air filtration is a key area in the prevention of sulfidation corrosion. According to McCreath (29) the compressor of the gas turbine engine will remove 96% of the salt that enters into the engine. He states that "there seems little doubt that the compressor of real engines can act as a massive filter". However, under idle to full power acceleration conditions, the compressor is capable of shedding. The salt shed from the latter stages of the compressor consists primarily of sodium sulfate.

### c. Sulfidation Corrosion Mechanisms

It is generally agreed that sulfidation corrosion occurs in the presence of a fused salt. DeCrescente and Bornstein (20) were among the first to experimentally demonstrate that mixtures of gaseous  $\text{Na}_2\text{SO}_4$  and air are relatively innocuous. A prerequisite for sulfidation corrosion is the presence of condensed  $\text{Na}_2\text{SO}_4$  (20). Bornstein et al (29) then demonstrated that the accelerated rate of oxidation of the sulfur rich alloy depleted zone is not responsible for the accelerated rate of oxidation associated with sulfidation corrosion (64,65) and then in a series of publications defined the role of the alkali constituent (30,31). Fig. 2. Accelerated oxidation is due to the inability of the substrate to form a protective oxide scale in the presence of oxide ions. They also demonstrated that alkali carbonates and nitrates cause the rate of oxidation of nickel base alloys to markedly increase as if they were coated with  $\text{Na}_2\text{SO}_4$ . The only exception is the absence of sulfide precipitates. Later, Johnson (32) et al demonstrated that for Co-W and Co-Mo alloys, a coating of  $\text{Na}_2\text{CO}_3$  had much the same effect as  $\text{Na}_2\text{SO}_4$ .

There have been many reviews of the mechanisms of sulfidation corrosion (33-35). Firstly, it should be noted that Hancock (36) called attention to the chemical-mechanical breaking of the normally protective oxide scale thereby allowing the corrosive  $\text{Na}_2\text{SO}_4$  salt to contact the substrate. He listed the following possibilities of scale failure.

- a. dissolution
- b. local reduction due to carbon
- c. erosion
- d. mechanical faults
- e. thermal stresses
- f. superimposed operating stresses and
- g. scale failure through reaction with chloride



The most general mechanism quoted for sulfidation corrosion is the salt fluxing model initially suggested by Bornstein and DeCrescente (37) and further extended by Goebel and Pettit (38,39). Essentially the model notes that oxides are relatively insoluble in stoichiometric sodium sulfate, but dissolve as anionic species in basic salt ( $\text{Na}_2\text{O}$ -rich) or as cations in acid salt ( $\text{SO}_3$ -rich).

Rapp and his co-workers measured the oxide solubilities in molten sodium sulfates (40-43) and described a mechanism similar to that of Goebel and Pettit but differed in that they do not require the sulfide forming reactions. Shores (44) reviewed the findings of the above and concluded that because the film of fused salt was very thin acidic dissolution cannot lead to fluxing. Luthra (45) believes that the role of  $\text{SO}_3$  is not to produce an acidic salt but to stabilize the low melting point solution of  $\text{Na}_2\text{SO}_4$  and the substrate sulfate. Lastly, it should be noted that Bessen and Fryxell stated that small amounts of carbon in the salt deposit could accelerate the corrosion by as much as a factor of ten-fold (44) and Smeggil et al (45) demonstrated that the morphology of Type II corrosion can be duplicated by the addition of carbon to the fused  $\text{Na}_2\text{SO}_4$  melt.

#### d. Sulfidation Inhibition

Investigators at UTRC constructed a reversible high temperature galvanic cell and demonstrated that oxides such as chromia react with and reduce the oxide ion content of molten sodium sulfate (66). In laboratory tests they demonstrated that the addition of finely divided chromia inhibited the accelerated oxidation of alkali coated nickel base superalloys. They also demonstrated that similar reductions in the corrosiveness of sodium sulfate coatings could be obtained with additions of  $\text{MoO}_3$ ,  $\text{V}_2\text{O}_5$  or  $\text{SiO}_2$  to the salt and demonstrated that a Ni-4Mo alloy corroded less when coated with sodium sulfate than commercially pure nickel. (67) Morrow et al (68) also reported that for Ni-Cr-Al-Mo alloys, at a given aluminium content, the corrosion decreased with increasing

molybdenum content. Nevertheless, Peters (69) found that the addition of molybdenum to the nickel base superalloys decreases its resistance to sulfidation corrosion. The differences in observation are explained as follows. Bornstein et al (70) pointed out that it is important whether molybdenum is present in alloys in solid solution or in a second phase. Sulfidation initiates in superalloys which contain coarse refractory metal rich carbides where the precipitates intersect the metal surface. Morrow et al reported that special care was taken to insure that the molybdenum was present in solid solution.

Based upon the success of the laboratory burner rig and engine tests, researchers at UTRC formulated a fuel soluble chromium compound for field tests. Full scale tests were conducted on the FT4A-12 engines aboard Sea Train line's GTV (Gas Turbine Vessel) Asia freighter and Euroliner, in the industrial FT4 engines of the Philadelphia Electric Company at Eddystone and in the PT-6 engines used in CN Turbo Train which operated between Montreal and Toronto, Canada (71,72). In all cases the fuel additive successfully attenuated sulfidation corrosion but the system was not problem free. The fuel additive and its injection system added to the overall costs. Due to economic consideration which include fuel cost differentials, the marine gas turbine engines were replaced by conventional diesels. A different problem was encountered with respect to CN turbo train. The addition of the fuel additives modified the viscosity of the fuel and in the colder weather of winter the formation of erosive carbon introduced a new problem.

## 2. Vanadium Corrosion

Vanadium is not an impurity found in distillate fuels, but may be found in residual and crude fuel oils. The vanadium is usually present as a porphyrin or other organometallic complexes but inorganic compounds of vanadium have also been reported (Ref. 46). During combustion of the fuel, the vanadium will react with oxygen to form an oxide. In the vanadium-oxygen system there exists at least four oxides, VO,  $V_2O_3$ ,  $V_2O_4$  ( $VO_2$ ) and  $V_2O_5$ , and whereas the first three can be considered as

refractory oxides (melting points in excess of 1500°C), the melting point of  $V_2O_5$  is approximately 670°C (47). Thus, vanadium pentoxide is a liquid at gas turbine operating temperatures.

Vanadium induced hot corrosion has been studied over the past four decades, however, most investigators include alkalis in their study since sea water contamination and alkali impurities are common in residual and crude oil fuels. Nevertheless it is important to differentiate the separate effects of (a) vanadium hot corrosion, (b) sodium sulfate hot corrosion and, (c) vanadium-sodium hot corrosion.

a. Gaseous  $V_2O_5$

The effect of gaseous  $V_2O_5$  on the oxidation behavior of nickel base superalloys and their protective alumina forming coatings has not been extensively studied, in part due to the wide variation in values of the saturated vapor pressure of  $V_2O_5$  available in the literature, Fig. 3 (48-53). The differences between the data may be due to (a) reactions between the liquid  $V_2O_5$  and the containment material and (b) effect of partial pressure of oxygen. Nevertheless, using the data of Suito (52) which gives the lowest volatility for  $V_2O_5$ , and assuming that equilibrium is achieved in the bulk gas, vanadium would only deposit on surfaces at 1450°F(787°C) and 1630°F(887°C) when the vanadium concentration in the fuel exceeded 21 and 110 ppm, respectively.

Fitzer (54) has shown that the rate of oxidation of copper and chromium is increased when these metals are exposed in an environment containing  $V_2O_5$  vapors. Bornstein et al studied the effect of gaseous  $V_2O_5$  on the oxidation of a nickel base superalloy and on intermetallic compound NiAl and reported that although  $V_2O_5$  increased the apparent rate of oxidation of the substrates, the increase is modest and not catastrophic (55).

b. Condensed  $V_2O_5$ 

Studies of the interactions between  $V_2O_5$  and various metals and alloys has been made by Pantony and Vasu (Ref. 56), Sachs (Ref. 57), Greenert (Ref. 58), Fitzer (Ref. 54), McFarlane (Ref. 59), and Kerby (Ref. 60) and mechanisms are proposed in which the liquid  $V_2O_5$  is both an excellent flux and an easy path for oxygen diffusion. It is generally stated or implied that large quantities of the corroder are not necessary to accelerate and maintain linear rates of oxidation because a cyclic process is involved in which vanadates form at the slag-metal interface and  $V_2O_5$  is regenerated at the slag-air interface. Davin et al (61) tried to identify the different complex compounds which are formed during corrosion tests in vanadium-containing atmospheres, by mixing  $V_2O_5$  with various oxides and heating at 950°C for 2 hours. They identified the compounds formed by x-ray diffraction and concluded that the accelerated attack is due to the presence of low melting vanadates which behave both as effective fluxes to remove protective oxides and as diffusion media which allow the rapid transport of oxygen to the metal surface.

Bornstein et al studied the interaction of  $V_2O_5$  with (a) nickel, (b) cobalt, (c) nickel base superalloys and the intermetallic compounds, (d) NiAl and (e)  $Ni_3Al$  by (1) applying a thin film of  $V_2O_5$  or (2) the continual deposition of the pentaoxide onto the heated specimen. They found that nickel and the Ni-Cr alloys did not oxidize at catastrophic rates in the presence of  $V_2O_5$ . During the oxidation of  $V_2O_5$  coated nickel, the rate of oxidation of the substrate was controlled by diffusion through either the NiO scale or the refractory vanadate phase separating the oxide from the melt. Similar results were noted for the cobalt except that the scales exfoliated when the specimens were removed from the furnace. However, the oxidation behavior of the  $V_2O_5$  coated NiAl,  $Ni_3Al$ , NiTi, B-1900, IN-100 and U-700 specimens differed markedly from that observed for the  $V_2O_5$  coated nickel, nickel-chromium and cobalt specimens. Whereas for the latter a protective scale formed separating the liquid oxide from the substrate, no protective phase was formed on the former.

It was concluded that the product of the reaction between  $V_2O_5$  and alloys which form alumina or titania rich scales is glass-like or amorphous.

### 3. Condensed Alkali-Vanadates

The predominant species in the salt deposit forming on gas turbine surfaces that burn vanadium containing fuels and operating in marine environments are expected to be  $Na_2SO_4$ ,  $V_2O_5$  and  $Na_2V_2O_6$  (23). Greenert reports that the most corrosive composition is a mixture of 79 m/o  $V_2O_5$ -21m/o  $Na_2V_2O_6$  (58). On freezing this has the composition  $Na_2O \cdot xV_2O_4 \cdot (6-x)V_2O_5$  (62). Sidky et al (63) report that the addition of  $Na_2SO_4$  to alkali vanadate melts enhances the rate of depletion of chromium from the alloy surface and the amount of internal sulfidation of chromium, aluminium and titanium in the alloy. Moreover, the leaching of the chromium by the vanadium allows the penetration of the melt further into the alloy for more sulfidation to take place. Seiersten and Kofstad (62) studied the vanadate corrosion of MCrAlY coated Inconel 600 and found that in the presence of molten alkali vanadates, the normally protective scales of  $Cr_2O_3$ - $Al_2O_3$  fail to develop. The alkali vanadate phase fluxes the oxide scale. It has been reported that nickel oxide inhibits the accelerated oxidation of  $V_2O_5$  through the formation of the refractory orthovanadate  $Ni_3(VO_4)_2$ , but these investigators found that NiO was selectively fluxed in melts containing sodium vanadate. Similar results are reported by Jones and Williams (73) who note that a surface layer of  $Co_2V_2O_7$  formed on CoCrAlY coatings could temporarily reduce corrosion rates by acting as a barrier against  $SO_3$  or through the reduction of  $V_2O_5$  activity within the corrosion phase.

Lastly, it should be noted that thermal barrier coatings are being evaluated for use in high temperature gas turbine engines. Levine (74) reports lifetimes in excess of 10,000 cycles when burning clean fuels. In contrast when 5 ppm of sodium and 2 ppm of vanadium are added to the fuel, lifetimes are less than 100 cycles. A. S. Nagelberg (75) examined the relationship between phase stability and alkali salts and concluded that

sodium vanadate enhances surface destabilization of zirconia structures by the leaching of the stabilizer. The subsequent phase transformation from the tetragonal to the monoclinic structure produced a porous material.

#### 4. Deposition and Inhibition

Corrosion of gas turbine components depends in part on the amount and composition of the impurity deposits on the surface. These deposits form as a result of impaction as well as condensation of impurities included in the gas from the fuel and air.

Luthra and Spacil performed a thermochemical analysis of the deposits formed from liquid fuels containing sodium and vanadium. They reviewed the earlier work of Halstead (76, 77) who concluded that even at 0.1 ppm V, fumes of  $V_2O_4$  may form at 1450°C. According to Halstead, vanadium occurs in residual fuel oil as an integral part of a porphyrin molecule, in which it exists in the divalent state. In the typical aero-type gas turbine combustor, Stevens et al (78) postulate that the vanadium in the fuel is exposed to temperatures of 1900-2000°K in the primary combustion zone where due to the low partial pressure of oxygen, is converted to the non-volatile  $V_2O_4$ . However, in the next stage of combustion, dilution air increases the partial pressure of oxygen and the gas temperature is reduced to about 1180°K. Under these conditions  $V_2O_5$  is the stable oxide and is relatively volatile. They conclude that a high carbon burden in the gas would limit the oxidation of  $V_2O_4$  to  $V_2O_5$ . Luthra and Spacil conclude that even for fuels containing 1 ppm V and 2 ppm Na, salt deposits may contain about a mole percent of  $NaVO_3$ . For fuels containing up to 30 ppm V, vanadium rich liquid deposits are expected from 600 to 1000°C.

Early in the study of vanadic corrosion, it was recognized that the accelerated oxidation associated with the presence of liquid  $V_2O_5$  could be attenuated if the melting point of the reaction products could be raised above the use temperature. Others recognized the advantage of reacting the corrosive vanadium with another compound in order to form a very volatile product which would not condense onto power plant components. Still others sought to dilute the corrodent thereby rendering the deposit relatively innocuous.

The metal oxides of Group II of the periodic table were initially identified as prime candidates for attenuating the corrosion associated with  $V_2O_5$  because they could form refractory vanadates. At present, most of the oxides of the metals in the periodic table have been evaluated as vanadic corrosion inhibitors. The alkalis were evaluated as volatile vanadate formers and mixtures of silica and alumina were used as dilutents. Listed in Tables I-III are the names of some of the authors, systems investigated and patents issued relating to vanadium corrosion inhibition.

Although numerous additives have been evaluated, the most effective addition used to control vanadium corrosion is based on the formation of the refractory orthovanadate  $Mg_3(VO_4)_2$  Fig. 4. It is generally assumed that the ratio  $3MgO:1V_2O_5$  will give protection because of the higher melting vanadates, i.e.  $3MgO + V_2O_5 \rightarrow Mg_3V_2O_8$  but the former is based upon weight percent and the latter upon moles. As shown in Fig. 4, at the nominal 3/1 ratio there is a large excess of magnesia. Nevertheless as noted by many investigators, the inhibition of vanadic corrosion by magnesium compounds is often incomplete.

Magnesium is added in many forms. The least expensive is as a solution of epsom salt. It is assumed that within the engine, the  $MgSO_4$  will be roasted to form the oxide. An expensive form of magnesium is the fuel soluble naphthenate which according to some investigators (91) insures inhibition since the reactive constituents are always together.

Young and Hershey (79) were among the first to explain why Epson salt is an effective additive in laboratory and atmospheric burner rig tests and not as effective in the power plants. At atmospheric pressure and at the temperatures of interest, more than 50 w/o of the  $\text{MgSO}_4$  decomposes. However, at a pressure of 10 atmospheres, the percent decomposition is closer to 2%.

Khys-Jones et al (93) have shown that the efficiency of the magnesium inhibitor is decreased as the level of sulfur is increased. The reduction in the ability of  $\text{MgO}$  to inhibit vanadic corrosion is attributed to the sulphation of  $\text{MgO}$  to  $\text{MgSO}_4$  which causes a change in the  $\text{MgO}:\text{V}_2\text{O}_5$  molecular ratio and subsequent formation of corrosive molten vanadates.

Lastly, as previously stated, the alkali vanadates are very corrosive and the mechanism by which they render the normally protective oxide scale ineffective is not known. Young (92) is among the first of many investigators to state that in the presence of sodium, "The vanadium simply prefers to react with sodium rather than the magnesium addition".

## II. DISCUSSION

### Sulfidation Corrosion

The increases in efficiency and performance of the gas turbine engine in the late fifties and sixties were due in part to advances in the development of nickel base superalloys. The temperature capabilities and mechanical properties of the alloys were significantly improved as the volume fraction of gamma prime was increased, which was accomplished in part by the reduction of the chromium content of the alloy. These changes altered the chemical properties of the alloy. Although oxidation is an important factor in material selection, coatings were developed to impart oxidation resistance. Nevertheless, as temperatures increased and alloy chemistry changed, a very aggressive form of accelerated oxidation was encountered.



This accelerated oxidation, called sulfidation attack requires the presence of a condensed salt rich in alkali sulfates, and this type of corrosion is most prevalent in marine and industrial gas turbines but also encountered in aircraft gas turbines. The source of the alkali components is generally believed to be sea salt crystals, born at air-sea interface and capable of traveling inland more than two hundred miles with the prevailing winds. In addition, marine and industrial fuels can be contaminated with sea water. Sulfur is a common impurity in liquid fuels and is a constituent of sea salt.

Although sulfate is the product of the reaction between sodium chloride, and the oxides of sulfur, and although there is good agreement between maximum deposition rates predicted by mass transport considerations and the experimentally observed deposition rates in laboratory experiments, it is most significant that the composition of the salt found on surfaces of the compressor is similar in composition to that found on the surfaces of the hot turbine components even though the salt has not passed through the burner nor encountered another source of sulfur. Moreover, the incidence of sulfidation corrosion in industrial gas turbines burning oil or natural gas (which is free of sulfur) appears to be related more strongly to the distance of the plant to the ocean rather than the presence or absence of sulfur in the fuel (94). It is therefore concluded that with respect to industrial and marine gas turbine, deposition from the gaseous state is important, but the principal source of the corrosive sulfate is the compressor of the engine.

Over the past two decades, significant improvements have been made to air filtration equipment. The single and two stage filtration system which, depending upon the relative humidity, allowed passage of "wet" particles into the engine is now replaced by three stage filtration units which prevents re-entrainment of water droplets. However, the efficiency of these units is still a function of engine power (air velocity through the system), and it is still observed that under some conditions, it is possible for droplet sizes less than 10 microns to escape filtration and enter into the compressor. Of the salt entering the compressor, less than six percent will leave. The remainder retained is released as the engine periodically sheds. Nevertheless, there is little doubt that the significant increase in life of marine and industrial turbine components is attributed to the superior filters and further increases are forthcoming as the ability of the filtration system to capture smaller and smaller diameter particles of salt improves.

The increase in life of industrial and marine gas turbine components is also attributable to the development and use of alloys modified specifically for improved resistance to sulfidation corrosion. The family of nickel base superalloys which include IN-713, B-1900, Mar-M-200 and IN-100 are still used in aircraft gas turbine engines but have been replaced in industrial and marine engines by alloys such as IN-939, IN-792 and IN-738. These high strength nickel base superalloys contain significantly higher concentrations of chromium and, based upon laboratory burner rig tests and field experience, are more resistant to sulfidation attack. Nevertheless, the selection of turbine materials is a compromise between mechanical and corrosion performance. In general, additional corrosion resistance for operation in hostile environments is provided by the use of the protective coatings.

The protective coatings are divided into two broad categories; aluminides and overlays. The aluminide coatings are formed by the reaction of the superalloy with a source of aluminum to form the intermetallic compound  $\text{NiAl}$ . Through control of temperature and aluminum activity, the coating can be made to grow primarily by the diffusion of aluminum into the substrate or by the diffusion of substrate elements to the free surface where they unite with the arriving aluminum atoms. In either case, the composition of the aluminide coating is dependent upon the chemistry of the substrate and therefore the substrate alloy affects the chemical properties of the aluminide coating.

The platinum-modified aluminide coatings have become the accepted standard for non-aircraft turbine hot section components. It is generally believed that the thin layer of electrodeposited precious metal influences the rate and concentration of substrate alloy constituents in the aluminide layer, thereby affecting the corrosion properties of the coating. The precious metal aluminides are reported to possess good resistance to Type I sulfidation and the debate is still in progress with respect to Type II corrosion.

The overlay coatings are based upon  $\text{MCrAlY}$  systems where M is iron, nickel and cobalt in varying proportions. The coatings can be applied by electron beam vapor deposition, sputtering, plasma spraying (air or vacuum) and cladding. A specific advantage of the overlay is that the composition of the coating can be made truly independent of the substrate alloy.

In general, the overlay coatings have exhibited the best resistance to Type I sulfidation corrosion and are the center of debate with respect to Type II. The general trend is to increase the chromium content of the coating to improve Type II corrosion resistance. A shortcoming of these coatings is that as the chemistry of the coating differs significantly from that of the substrate, the tendency for interdiffusion to occur increases with increasing temperature. Thus, the coatings most resistant to Type II corrosion are limited with respect to temperature.

Further improvements in the oxidation and hot corrosion resistance of advanced gas turbine materials is anticipated with the growth of the single crystal alloys, which do not contain any of the precipitated refractory rich carbide phases commonly associated with initiation of sulfidation corrosion. Moreover, the single phase low sulfur aluminide coatings first described in a study conducted for ONR, and now being brought to fruition in a NADC program are anticipated to further improve oxidation and sulfidation resistance.

The salt fluxing models have been the basis of much of the analysis of sulfidation corrosion over the last ten years, with emphasis on Type II corrosion and acid fluxing. The acidic model explains in part the dependency on the partial pressure of  $\text{CO}_2$  and explains why the addition of  $\text{V}_2\text{O}_5$  to  $\text{Na}_2\text{SO}_4$  eventually promotes attack. However, the addition of  $\text{NaVO}_3$  to the salt to give the same Na/V ratio produces the same accelerated rates of oxidation although it is not apparent how it affects the acidity of the salt.

Shores suggests that the important factor in Type II sulfidation corrosion is the impregnation of the porous scale by the salt. He points out that the overall corrosion rate is so rapid that there can be essentially no continuous layer of oxide between the porous salt-impregnated layer and the metal. The transport of oxygen is down the larger pores, and it diffuses into the salt normal to its thickness.

Ried was among the first to note the relationship between low melting pyrosulfates and superheater corrosion. Luthra states the role of the external  $\text{SO}_3$  partial pressure required for Type II corrosion is to stabilize the low melting point solutions of  $\text{Na}_2\text{SO}_4$  and  $\text{CoSO}_4$ . According to Luthra the initial stage of Type II is the formation of a liquid Na-Co sulfate and in the propagation stage,  $\text{SO}_3$  migrates inward as the cobalt migrates outward through the liquid salt.

Finally, it should be noted that Type II corrosion is most frequently associated with reduced power operation. This condition could favor carbon formation. According to McCreath, gas phase formation of carbon generates particles up to about 10nm which may coagulate to form larger masses. Smeggil et al identified carbide formation in the outer layer of aluminide coatings. No carbides were present in the mid-section of the coating although carbides are typically present at the coating substrate interface. Smeggil concluded that the source of carbon for the outer carbides is not the substrate alloy. Moreover, Smeggil and his co-workers have reproduced the Type II morphology in the laboratory by impinging carbon particles onto sodium sulfate coated substrates. The interaction between carbon and sodium sulfate could produce localized high partial pressures of  $\text{SO}_x$  but could also produce a very basic fused salt. In view of the role that particulate carbon could play in the vanadic corrosion (soon to be discussed), and the pitting nature of Type II attack, the role of carbon with respect to sulfidation corrosion should be investigated.

### Vanadium Corrosion

Vanadium oxide like the alkali sulfates can accelerate the rate of oxidation of gas turbine alloys. In considering vanadic corrosion, attention must be focused on the corrosive nature of the pentoxide as well as the alkali vanadates. Whereas gaseous mixture of air and sodium sulfate are relatively innocuous, gaseous  $V_2O_5$  has been shown to increase the rate of oxidation of (a) nickel base superalloys and (b) the intermetallic compound NiAl which is the basis of the protective coatings used to extend the life of turbine hardware. The increase in rates of oxidation, as reported by Bornstein, is modest and not catastrophic. Nevertheless, there is insufficient data to establish the magnitude of the increase in rates of oxidation nor the long term effect.

The effect of liquid vanadium oxides and mixtures of  $V_2O_5$  with metal vanadates on the oxidation behavior of various metals and alloys has been studied for more than four decades. It is known that catastrophic corrosion occurs when a liquid phase rich in vanadium is present and that a large number of vanadate systems have eutectics with melting points less than  $600^\circ\text{C}$  and the presence of  $\text{SO}_2(\text{SO}_3)$  can further lower the temperature at which liquation can occur. Studies have been conducted between  $V_2O_5$  and various metals and alloys and it is believed that liquid  $V_2O_5$  is both an excellent flux and an easy path for oxygen diffusion.

A conclusion based upon the results of immersion tests is that the rate of oxidation of the test specimen is linear with respect to time. This result should not be surprising since the volume of liquid greatly exceeds the volume of alloy in test. Nevertheless,  $V_2O_5$  does form low melting eutectics, peritectics and some moderate and refractory congruent melting point compounds as shown in the table below.

Oxide	Eutectic		Pertectics		MP of Refractory	
	°C	m/o	Number	Temp.	Vanadate	°C
$\text{Al}_2\text{O}_3$	658	1.46	none		$\text{AlVO}_4$	decomposes
$\text{FeVO}_4$	635	15	1	840	$\text{FeVO}_4$	840°
$\text{Cr}_2\text{O}_3$	655	25	1	902	$\text{CrVO}_4$	902
NiO	650	22	3 $\text{NiV}_2\text{O}_6$	750	$\text{Ni}_3\text{V}_2\text{O}_8$	1210
			$\text{Ni}_2\text{V}_2\text{O}_7$	850		
			$\text{Ni}_3\text{V}_2\text{O}_8$	1210		

It is doubtful that within gas turbine engines sufficient quantities of  $\text{V}_2\text{O}_5$  could accumulate onto rotating turbine components producing conditions similar to the immersion tests used to determine rates of dissolution of turbine alloys in the liquid pentoxide.

It has been demonstrated that nickel and nickel-chromium alloys can form protective vanadate scales which limit the availability of both oxygen and liquid  $\text{V}_2\text{O}_5$  to the metallic substrate. Moreover, at 900°C the loss of weight of  $\text{V}_2\text{O}_5$  coated nickel is related to the rate of evaporation of  $\text{V}_2\text{O}_5$  from the surface. However, the nickel base superalloys and the coatings used to extend the life of turbine components do not form nickel oxide rich scales, but form alumina rich scales.  $\text{V}_2\text{O}_5$  reacts with alumina to form glasses, therefore liquid  $\text{V}_2\text{O}_5$  is expected to be very corrosive with respect to the advanced alloys currently used in gas turbine engines.

Although liquid vanadium pentoxide will accelerate the rate of oxidation of current gas turbine materials it is possible to attenuate or inhibit the corrosive attack by condensed  $\text{V}_2\text{O}_5$  by (a) preventing the deposition of  $\text{V}_2\text{O}_5$  and/or (b) reacting the  $\text{V}_2\text{O}_5$  with an oxide to form a refractory vanadate. Vanadium can be made innocuous by preventing its oxidation from the solid tetroxide to the low melting corrosive pentoxide. It can also be made innocuous through the formation of refractory vanadates which are not subjected to sulphation reactions.

Stevens and Tidy (95) indicated that within the aero-type gas turbine combustor, the vanadium in the fuel is oxidized to the pentoxide via a two step process. They stated that in stage I, where the temperature is highest and the partial pressure of oxygen low, the vanadium is converted to the non-volatile tetraoxide,  $V_2O_4$ . Later, at lower temperatures and higher partial pressures of oxygen is the  $V_2O_4$  oxidized to the pentoxide.

The same investigators also demonstrated that the vanadium deposition rate was dependent upon the combustion efficiency of the burner. Under "good" combustion conditions (7-13 mg  $m^{-3}$  carbon in the exhaust) the rate of deposition of  $V_2O_5$  was significantly lower than under "poor" combustion conditions (40-60 mg  $m^{-3}$  carbon in the exhaust). They attribute the differences in the measured deposition rates due to the presence of larger amounts of carbon in the deposit which would tend to prevent the oxidation of the deposited  $V_2O_4$  to  $V_2O_5$  and therefore slow the rate of evaporation of the more volatile  $V_2O_5$ .

Surprisingly the rate of deposition of  $MgO$  was greater than that of  $V_2O_5$ . The magnesium was added to the fuel as a soluble naphthenate (just like the vanadium) so that in the combustion process similarly sized particles would be expected to form. At UTRC, investigators dissolved metal naphthenates in JP-5 fuel and measured the deposition rate of the oxides. It was found that the oxides of  $Y_2O_3$  and  $NiO$  did not adhere to the surfaces of the spinning test specimens. However, deposits rich in magnesium were formed whenever magnesium naphthenate was used (90). It was concluded that the presence of the sulfates provided the "stickiness" necessary for particle adhesion. Similar results were reported by Laxton et al (97) who found that there was a ten-fold increase in the deposition of magnesium when vanadium was present in the fuel and concluded that the presence of liquid  $V_2O_5$  enhanced retention of the magnesium particles.



Drake and Hanett studied the effects of gas born carbon as it affects oil ash corrosion of superheaters and noted it is possible to decrease corrosion by modifying the combustion process such that a thin film of carbon deposits.

Carbon is a reducing agent with respect to  $V_2O_5$ . As previously noted, a distillation process occurs during the combustion of the vanadium containing fuel. Initially the lighter fraction vaporizes and burns thereby concentrating the vanadium in the carbon rich char particle. It is therefore suggested that through a better understanding of a combustion and deposition process, the vanadium rich particles can be made to pass harmlessly out of the engine as the involatile  $V_2O_4$  instead of the corrosive liquid pentaoxide. It is realized that carbon may have an effect on alloy corrosion resistance and carbon produced in the combustor could result in an erosion problem. The recommendation does include the re-examination of the role of carbon with respect to low temperature (Type II) sulfidation corrosion, and defining the partial pressures of oxygen necessary to stabilize vanadium as the tetraoxide.

Vanadium pentoxide will react with many oxides to form high melting point compounds. At present, magnesium is the most popular additive used to attenuate vanadium corrosion. The oxides of the elements of magnesium, zinc, calcium, aluminum, barium, nickel, cobalt, iron, as well as mixtures of silica and magnesia and the mixtures containing aluminum plus magnesium and silicon in certain proportions have been investigated and patented. In the late fifties and early sixties, patents were issued for the addition of alkalis and sea water to attenuate vanadic corrosion. The use of sodium salts to attenuate vanadium oxide corrosion will be discussed. However, as first noted by Young, the stability of  $MgSO_4$  is pressure dependent and as more recently noted by Rhys-Jones, the sulphation of magnesia is dependent upon the partial pressure of  $SO_x$ .

NiO reacts with  $V_2O_5$  to form a refractory vanadate and many refractory vanadates are formed by the reaction of the lanthanide oxides with  $V_2O_5$ . Moreover, nickel has been identified as a potential additive, and can be found as an impurity in certain crudes that contain vanadium. Radcliff reports that no corrosion was noted when the deposits were removed from turbine components from a gas turbine engine fired on crude oil. The deposits were identified as nickel pyro and orthovanadate. However, the relative stability of the oxides of the lanthanides as well as NiO with respect to sulphation and vanadate formation need to be determined.

#### Vanadium-Alkali Corrosion

There are economic advantages associated with burning lower cost residual and certain crude oils, but the corrosive deposits rich in alkali and vanadium promote hot corrosion and negate the savings in fuel costs.

As previously stated vanadium pentoxide can react with alkali salts to form a series of complex vanadyl vanadates often termed bronzes and described by the formulas  $Na_2O \cdot xV_2O_4 \cdot (6-x)V_2O_5$  and  $5Na_2O \cdot xV_2O_4 \cdot (12-x)V_2O_5$ . It is known that when the sodium to vanadium ratio is low the composition of the deposit consists primarily of the vanadate  $(Na_2O)_x \cdot V_2O_5$  however the deposit can be converted to  $Na_2SO_4$  when the partial pressure of  $SO_3$  is relatively high (1KPa at 650°C). It is also known that  $V_2O_5$  and the low-sodium vanadates are n type semiconductors; and as the alkali content increases, they become ionic conductors.

It is known that the rate of oxidation of alkali vanadate coated nickel base superalloys is comparable to that of the  $Na_2SO_4$  coated alloy but the chemistry associated with the oxidation process is not known. It is known from the results of experiments conducted for more than three decades that various compounds based upon the group IIa & b, and the transition elements, alone, or in combination with silicon and or aluminum, do not attenuate the corrosion associated with deposits containing alkali and vanadium compounds. According to Bornstein who reviewed the available thermodynamic data, the

products of the reaction between magnesium orthovanadate and sodium sulfate are sodium meta vanadate and magnesium sulfate. As stated by Young, vanadium simply prefers to react with sodium rather than magnesium. It is known that the transition metals, oxides such as NiO form refractory vanadates when they combine with liquid  $V_2O_5$ , however as most recently reported by Seversten, NiO is selectively fluxed by sodium vanadate. It is known that the addition of alkalis as naphthenates or sea water has been used to attenuate vanadium corrosion. It is now realized that this form of corrosion control is quite limited, based upon the formation of the volatile alkali vanadates; and in the current family of gas turbine engines would promote sulfidation corrosion.

Coatings are also a means of imparting corrosion resistance. Metal temperatures within the gas turbines are steadily increasing and coatings which differ significantly in chemical composition from the substrate are subject to interdiffusion with the substrate altering the chemistry of the coating and the mechanical and physical properties of the substrate. Thermal barrier coatings are being employed in advanced aero engines. However, vanadium compounds can leach the oxides used to stabilize these ceramic coatings thereby limiting the life of the coating.

### III. RECOMMENDATIONS

Through the understanding of the mechanism(s) by which hot corrosion occurs, it is possible to modify or alter a critical step and thereby attenuate the corrosion process. A prerequisite for sulfidation corrosion is the presence of the alkali salt  $Na_2SO_4$ . Attenuation is physically achieved through the use of sophisticated filtration and wash systems thereby (a) minimizing the deposition of the salt or (b) hastening its removal prior to the onset of corrosion. Attenuation is also achieved by chemical changes in the salt through the use of fuel additives or modifications to the chemistry of the alloys and coatings. Examples are the use of a chromium base fuel additive, alloy modifications and the enrichment of chromium in the

coatings. However, the problem with respect to vanadium accelerated corrosion is more complex.

The difficult problem is not only the corrosion associated with gaseous and condensed vanadium pentoxide, but also the corrosion associated with the complex vanadium compounds of the alkali family which exist over wide chemistry ranges and melting points. Moreover, the alkali vanadates are stable compounds which tend to dissolve the oxides that form on superalloys and aluminum rich intermetallic compounds.

In order to negate vanadic corrosion, it is recommended that the complex problem be divided into smaller steps, and from an understanding of the individual corrosion phenomena, determine and construct the overall corrosion model in which the critical step necessary to attenuate the hot vanadium corrosion can be identified.

The recommended steps include but are not limited to (a) gaseous and (b) condensed oxides and (c) the chemistry of the alkali-oxide interactions as it pertains to gas turbine materials, as outlined below.

- I. Combustion, Deposition and Erosion
- II. Alkali-Vanadium Chemistry
- III. Surface Chemistry - Substrate-Corroden Interactions

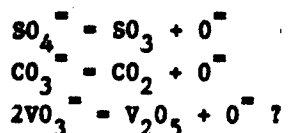
In order to understand or model deposition it is necessary to be able to describe the chemical and physical state of vanadium compounds prior to deposition. The chemical/physical state of vanadium during deposition may depend on the initial structure of the fuel-bound vanadium as well as the combustion process. For example, based upon collision theory, the half-life for the formation of a  $V_2O_4$  dimer formed from a fuel containing 10 ppm vanadium is on the order of a millisecond. The residence time in the advanced combustors of current engines is only a few milliseconds. Therefore, it is unclear if the turbine components interact with deposits on the order of 10A or are bathed in a gaseous stream. Moreover, enhanced collision rates are possible due to the existence of charged species/

particles or to induced dipole effects. Alternately interactions with soot particles or species could artificially enhance condensation and affect oxidation states of the condensate. Lastly, modifications to the combustion process to influence condensation and condensate chemistry could promote or initiate erosion/corrosion problems; the severity of which is material dependent. These are some of the important considerations that must be addressed.

Alkali salts interact with oxides of vanadium to form a family of compounds call "bronzes". The source of the alkali is the periodic shedding of the compressor, the sea of chloride rich particles that continually pass through the compressor and the sea water that contaminates marine fuels. Poorly understood is the chemistry of the reactions between the aforementioned sources and the vanadium rich combustion products of the fuel. This knowledge may prove invaluable in the formulation and understanding of the behavior of a fuel additive to influence the ionic character of the molten salt or to react and form refractory (solid) products.

The chemistry of the reaction between liquid  $V_2O_5$  and the transition metals is fairly well documented. Nickel oxide can combine with  $V_2O_5$  to form the refractory vanadates which then separates the molten oxide from the metal substrate. In a similar manner the lanthanide series also form refractory vanadates, and the experimental data strongly suggests that these compounds would be the logical basis for fuel additives. In fact, Mother Nature does add fuel soluble nickel to many crude oils which contain vanadium and it is often reported that no corrosion is observed beneath the deposit of nickel vanadates. However, the alloys of the earlier era were based on the Ni-Cr system and did not form the alumina rich scales that now develop on the alloys. It has been demonstrated that vanadium pentoxide is a strong glass former and alumina (and titania) are glass extenders. Little is known about the chemistry of the reaction between vanadium pentoxide and aluminum and the subsequent formation of glasses which dissolve the oxide scales needed for alloy substrate protection. It is therefore recommended that this knowledge base be determined.

The last important area that needs to be examined is the corrosion associated with the presence of the alkali vanadates. It is established that the alkali salts of the sulfate can dissolve the normally protective oxide scale that separate fused sodium sulfate from the superalloy substrate, and that the kinetics of this reaction can be influenced by the addition or subtraction of oxide ions through the use of external oxides or reactive elements which enters into or becomes part of the oxide scale. Chromium oxide,  $\text{Cr}_2\text{O}_3$ , reacts with and in effect controls the oxide ion content of sodium sulfate. In a similar fashion, chromia influences the corrosion of fused sodium carbonates. It is not clear, however, if the corrosion associated with molten  $\text{NaVO}_3$  (or  $\text{Na}_3\text{VO}_4$ ) is similar to that of  $\text{Na}_2\text{SO}_4$  or  $\text{Na}_2\text{CO}_3$  since the product of the reaction for the former would be a liquid while that of the latter salts is a gas, i.e.,



It is therefore recommended that sequences of reactions that occur when  $\text{Na}_x\text{V}_y\text{O}_z$  reacts with superalloy components be defined similar to that performed by the alkali sulfates in order to determine the weakest link in this corrosion process.

In summary <sup>it</sup> appears possible to attenuate vanadium hot corrosion provided that it is recognized that the problem consists of two related corrosion phenomena. They are the accelerated oxidation of alumina forming materials by the glass forming vanadium pentoxide and the accelerated oxidation of these materials by fused alkali vanadates. Each may be present independent of the other or simultaneously in which case alkali sulfates may also be present. It is recommended that a research program be initiated aimed at obtaining: 1) A better understanding of the process by which the vanadium in the fuel is transferred to the surface of turbine components in order to assess the feasibility of preventing vanadic deposition, 2) Kinetic data and an understanding of the chemistry involved in the formation of the glasses that form on the surface of the advanced alloys and coatings when

R88-917873

-29-

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they are covered with a film of  $V_2O_5$  in order to cause devitrification through alloy modification or a fuel additive and (3) kinetic and thermochemical data for the accelerated oxidation of alkali vanadate coated gas turbine materials to identify the rate controlling process or weakest link so that appropriate changes can be made to the alloy or coating through a fuel additive to attenuate the corrosion. (AS)

Table I  
Additives for Vanadium Oxide Corrosion

<u>Author(s)</u>	<u>Year</u>	<u>Compounds</u>	<u>Ref.</u>
H. Fredricki, T. Eden	1955	ZnO, $Al_2O_3$ + Kieselguhr	82
B. King and L. Suber	1955	BeO, MgO SrO, BaO, $Al_2O_3$ $SiO_2$	81
G.W. Cunningham et al	1956	CaO, BaO, SrO MgO	83
W. Young and A. Hershey	1957	$Al_2O_3$ , MgO, CaO	79
K. Sachs	1958	MgO, CaO, NiO, ZnO, $Cr_2O_3$	57
Gulf Research Develop Center	1964	MgO, Sea Water, Sodium Naphthenate	84



B88-917873

Table II  
Vanadium Corrosion Control - Patents

<u>Patent #</u>	<u>Element(s)</u>	<u>Date</u>
2,949,008	Na, Mg	8/16/60
2,966,029	Sea Water	12/27/60
2,968,148	Zn	1/7/61
2,987,884	Ca	6/13/61
3,057,151	RE	10/9/62
3,078,662	Al	2/26/63
3,078,664	Alkalies	2/26/63
3,078,665	Ni, Co, Fe, Ni	2/26/63
4,328,285	CeO	5/4/82
3,817,722	SiO <sub>2</sub> x MgO	6/18/74
4,659,339	Al + Mg + Si	4/21/87

Table III  
Phase Studies - Vanadium Corrosion Control

<u>Systems</u>	<u>Author</u>	<u>Ref.</u>
$V_2O_5-Al_2O_3$ $V_2O_5-CaO$ $V_2O_5-Co_3O_4$ $V_2O_5-Cr_2O_3$ $V_2O_5-MgO$ $V_2O_5-CuO$ $V_2O_5-Fe_2O_3$ $V_2O_5-NiO$ $V_2O_5-BeO$ $V_2O_5-ZnO$	Lucas, Weddle & Preece	85
$MgO-V_2O_5$ $CaO-V_2O_5$ $CaO-MgO-SiO_2$	Eke and Brett	86
$Na_2O-V_2O_5$	Slobodin and Fotier	87
$V_2O_5-ZnO$	Pollard	88
V - O	Anderson	89
V - Y	Gambino and Guave	90
Cr-V-O; Al-V-O	A. Bardese	80

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R88-917873

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FIG. 1

# PROGRESS IN TURBINE BLADE MATERIALS

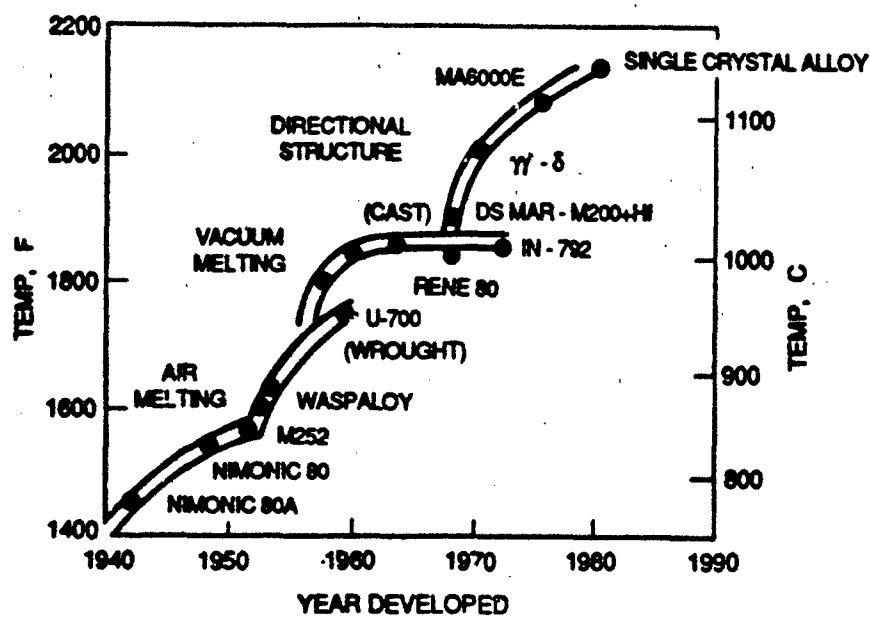


FIG. 2

# ALKALI SALTS ACCELERATE OXIDATION

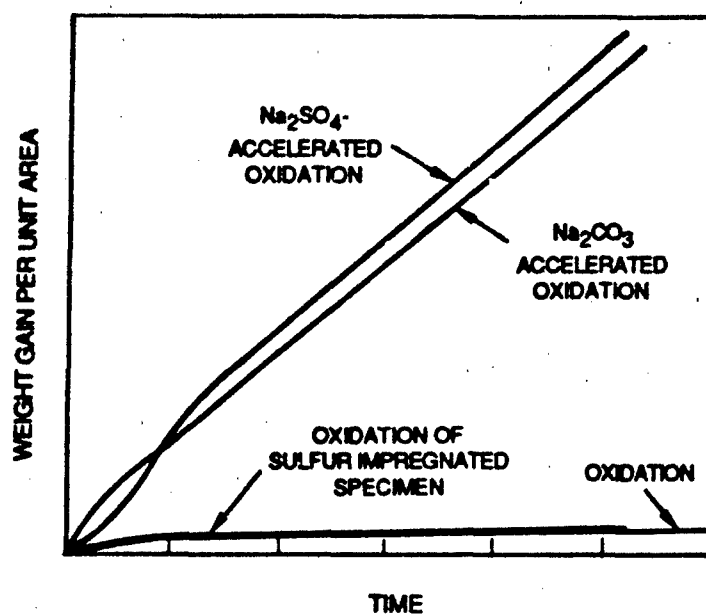


FIG. 3

# VAPOR PRESSURE OF $V_2O_5$

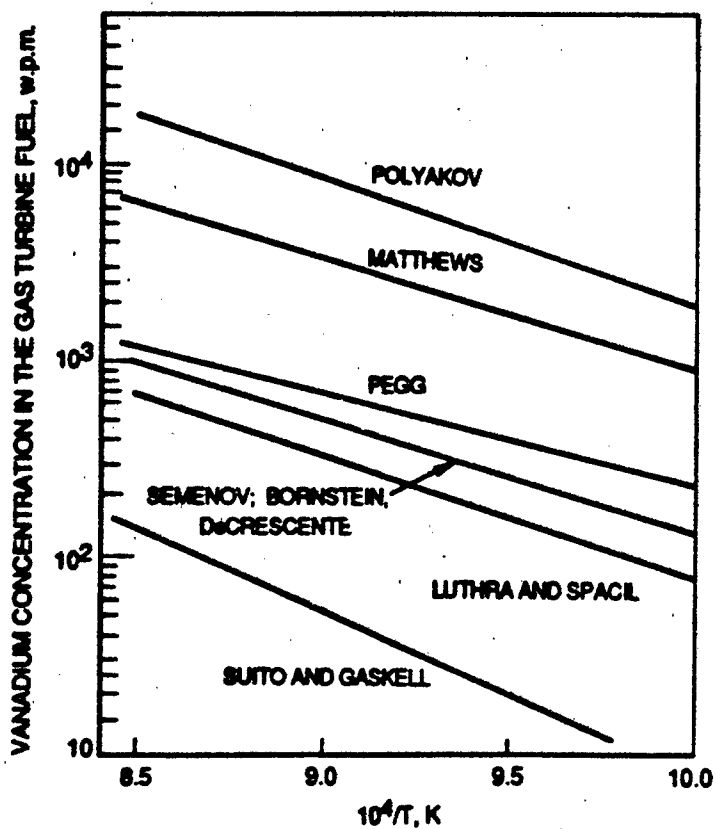


FIG. 4

**MgO - V<sub>2</sub>O<sub>5</sub> PHASE DIAGRAM**